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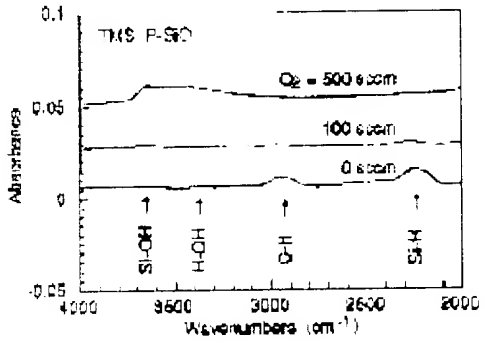
(71)Applicant HITACHI LTD
HITACHI ELECTRON ENG CO LTD
(72)Inventor : SAITO MASAYOSHI
HONMA YOSHIO
KUDO YUTAKA

(54) FORMATION METHOD OF SILICON OXIDE FILM

(57)Abstract:
PURPOSE: To form a silicon oxide film which is small in an OH content group and excellent in moisture permeability preventing properties and coated with a high offset.
CONSTITUTION: A mixed gas of an oxidizing gas containing alkoxy silane and hydrogen is introduced, thereby forming a silicon oxide film having an Si-H bonding based on a plasma CVD method. This makes it possible to manufacture a semiconductor device having a high density and high reliability multilayer wiring at low cost.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the manufacture method of a silicon oxide, and relates to the formation method by the CVD of the silicon oxide which insulates between the vertical wiring layers in the multilayer interconnection of a semiconductor device especially.

[0002]

[Description of the Prior Art] In formation of the silicon oxide for semiconductor devices by CVD, the mono silane (SiH4) has been used as a raw material from the former. However, in connection with the densification of a large-scale integrated circuit (LSI), the pattern size turned minutely, it became the stage where now submicron processing was performed, and some trouble has arisen. For example, it is SiH4 although the size of a wiring interval is becoming indispensable [the embedding of the quality insulator layer to the portion into which the ratio (aspect ratio) of the depth (height of wiring) to between wiring exceeds 1] by submicron one in the manufacture process of a multilayer interconnection. It is raised to such a detailed slot and the detailed level difference section of a high aspect ratio with the used CVD that sufficient insulator layer formation cannot be performed. Moreover, if it is going to dare apply, the problem of aluminum wiring being corroded and disconnected in permeation of the moisture from a portion in which the short circuit during wiring and covering nature were inferior will arise. Moreover, SiH4 When oxygen (O2) and the nitrous oxide (N2O) of a oxidizing gas are contacted, it is also a problem that it reacts easily and is easy to generate particle. Moreover, SiH4 It is self-ignition nature gas which will burn if ordinary temperature describes air, and when it mixes with ****** gas, it is a dangerous material which has explosivility. This SiH4 If in charge of use, employment which formed the facility in alignment with the regulations about a specific high pressure gas, and took care of safety enough must be performed, and the cost for it is also by no means cheap.

[0003] Above SiH(s)4 In order to conquer the fault of the used plasma CVD method, a tetraethyl ortho silicate (henceforth TEOS) is SiH4. It has come to be used as a changing raw material. The silicon oxide formed by the plasma CVD method using TEOS is SiH4. Excelling [and] the case where it uses in level difference covering nature, TEOS is a comparatively safe raw material which self-ignition nature does not have, either.

[0004] However, the silicon oxide formed by the plasma CVD method using TEOS has still left the problem by compactness, the transparency prevention property of moisture, and the content OH radical weight. SiH4 Compared with the silicon oxide which used as the source and was formed by the plasma CVD method, water resistance is inferior. Si-H combination hardly exists in a film, but this is considered because there are comparatively many OH bases. Moreover, polarity is large and a content OH basis enlarges the dielectric constant of a silicon oxide. Although OH basis can be reduced and a precise silicon oxide can be obtained if heat treatment of about 600-800 degrees C can be performed after film formation by the plasma CVD method using TEOS, since aluminum system wiring deteriorates, it is inapplicable. Furthermore, when it was going to form the fluid silicon oxide on the silicon oxide formed by the plasma CVD method using TEOS by the CVD which used an alkoxide and ozone, such as TEOS, there was a problem that a generation film front face served as the configuration where irregularity is intense, or the so-called ground dependency, like dispersion in the thickness of a generation film becomes large became remarkable.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the formation method of the silicon oxide which was excellent in the flat nature which solves simultaneously the technical problem about the reduction or the removal, and the waterproof improvement in OH basis in a generation film, the technical problem of high rank difference covering **** formation, and the technical problem that a ground dependency is abolished in film formation of ozone CVD.

[0006]

[Means for Solving the Problem] The above-mentioned technical problem is Si source and O2 so that oxidization gas, such as O2 or N2O, and mixed gas may be introduced using the alkoxide which has Si-H combination as the Si source and the abb sow [BANSU] ratio of Si-H/Si-OH in a generation film may become 1/3 or more. Or N2O It is solvable with a means to set up flow rate and to form a silicon oxide by the plasma CVD method.

[0007]

[Function] The alkoxide which has Si-H combination is used for this invention as the Si source. This kind of alkoxide acts so that there may also be no self-ignition nature at the time of acting so that high rank difference covering nature may be secured as a property common to an alkoxide, and touching air, since it had Si-O combination in the interior of a molecule, process safety may

be raised by leaps and bounds and the cost of a facility may be reduced, and it is SiH4. It acts so that it may compare and particle may also be reduced

[0009] Si-H combination included in Si source of this invention is incorporated also in a generation film by controlling oxidization gas to the flow rate of a proper field. Since the Si-H combination in this film works so that the trap of the moisture which is going to permeate may be carried out, it acts so that the transparency in the film of moisture may be prevented. Si-H combination which exists in a film front face works as an active site in which surface reaction occurs easily, and it acts so that the silicon-oxide formation reaction in a front face may advance. On the other hand, a surface Si-OH combination has strong polarity, and it tends to be connected with a carbon compound with the oxygen which is a product in reactant gas, and after this carbon compound has reached the front face, it acts so that surface reaction cannot advance easily and may become. Therefore, in order to perform uniform and high-speed film generation, it is effective that the Si-H point density in a front face is large, and it is large, the density of Si-OH combination is small, i.e., a Si-H Si-OH ratio. Since H or OH combines with most portions into which silicon combination was confused, when the Si-H combination in a film is made to increase, Si-OH combination has the property of decreasing. And according to the experiment, 1.3 or more generation films act so that transparency of moisture may be prevented, and the abb sow BANSU ratio of Si-H/Si-OH acts this film so that a ground dependency may be abolished in the ozone CVD as an underlay film

[0008]

[Example] The example of this invention is explained in detail using drawing. The structure of a plasma CVD room where it used for formation of a silicon oxide is shown in drawing 1. The case where trimethoxysilane (henceforth, TMS) is used for Si source is explained as an example. TMS was put into the container made from stainless steel with the liquid source, carried out bubbling of the nitrogen gas which is a carrier gas, and introduced it into the CVD room. The temperature of the container of TMS set the flow rate of 25 degrees C and conveyance nitrogen gas to 0.2slm(s). In order that the gas piping from a container to a CVD room might suppress adsorption and liquefaction of gas, it attached the temperature gradient and kept it at 60-100 degrees C. TMS and the mixed gas of O2 and N2 were put in from the gas induction 1, the substrate 4 with a diameter of 4 inches was placed on the lower electrode 3, and RF power was impressed between the up electrode 2 and the lower electrode 3. The frequency of RF set 50kHz and RF power to 100W. In addition, the up electrode 2 and the lower electrode 3 could set up the position independently, respectively, and the electrode spacing here set them to 12mm. The CVD room is equipped with the infrared transparency aperture 7 for analyzing reactant gas.

[0010] Next, the infrared absorption spectrum at the time of introducing TMS and being referred to as pressure 4 Torr was shown in drawing 2. This gas is the composition shown in drawing 2, and contains C-H, Si-H, and Si-O. Drawing 3 is the infrared absorption spectrum of the reactant gas of the plasma state which impressed RF (RF power: considering as the plasma state -- everything but introductory gas -- 1775cm-1 -- formaldehyde (HCHO) -- H2O by which CO2 stuck to the 2360cm-1 neighborhood to the 3740cm-1 neighborhood, and Si-OH combination stuck to the silica to the 3400cm-1 neighborhood moreover, the 3600cm-1 neighborhood and the 1600cm-1 neighborhood -- molecule-like H2O It accepts, although it is little.

[0011] Next, an example of the infrared absorption spectrum of the formed silicon oxide is shown in drawing 4. On the relation of a display, in oxygen 100sccm and 500sccm(s), 0.05 ******s of abb sow BANSU are set to 0.025, respectively, and it is shown. 1slm and oxygen set [pressure 1Torr, 12mm of electrode spacings, and the conveyance nitrogen gas of TMS / 0.2slm(s), the substrate temperature of 350 degrees C, and dilution nitrogen gas] membranous formation conditions to 0 - 500sccm. H2O to which Si-OH of the 3660cm-1 neighborhood and the 3400cm-1 neighborhood stuck when oxygen was 500sccm(s) It accepts and has become a spectrum configuration equivalent to the silicon oxide at the time of using TEOS as a raw material. When oxygen is 100sccm(s), abb sow BANSU of Si-OH decreases and Si-H is accepted in the 2200cm-1 neighborhood. When oxygen is set to 0sccm, a film grows. At this time, Si-OH decreases to a very small value, and abb sow BANSU of Si-H and C-H becomes large. Per abb sow BANSU of drawing 4 and also the result which measured the oxygen flow rate dependency in detail were shown in drawing 5 here. OH basis-related abb sow BANSU increases with the increase in an oxygen flow rate, and Si-H and C-H decrease with the increase in an oxygen flow rate. By changing the flow rate of TMS and oxygen, it was confirmed that the amount of the Si-H combination in the silicon oxide to generate or OH basis is changeable.

[0012] Triethoxysilane (TES) is in the material to which TMS and the property were similar. Although the same oxygen flow rate dependency as the case of TMS was shown when TES was used as Si source, when the same flow rate compared, the result that abb sow BANSU of C-H in a film was large 20 to 50% was brought.

[0013] Next, in order to evaluate the level difference section covering configuration at the time of using TMS, the cross section of the conditions from which the silicon oxide of a flat part is set to 300nm using a sample with a slot with a width of face [of 350nm] and a depth of 600nm was observed by SEM. Judging from the state of the overlaying of a level difference edge, when TMS is used as Si source, a configuration almost equivalent to the case where TEOS is used is acquired, and it is SiH4. It turns out that the configuration at the time of using is excellent.

[0014] Next, the oxygen flow rate dependency of the refractive index n of a generation film was shown in drawing 6. Although it is a value equivalent to the silicon oxide which used TEOS as the raw material when an oxygen flow rate is large, if an oxygen flow rate is decreased, a refractive index will increase. When an oxygen flow rate is 20 or less seems, the increase in a refractive index is remarkable.

[0015] 0.5% of next, concentration The result which measured the etch rate of a silicon oxide with dilution HF liquid was shown in drawing 7. Since it is usually 10 - 12 nm/min, the silicon oxides formed by the plasma CVD method which used as the raw material TEOS currently generally used for the multilayer interconnection of LSI are 2.5 nm/min of a thermal oxidation film. It is

a quite clear precise film. The etch rate increased slightly as it was shown in drawing 7, when the oxygen flow rate was made to increase.

[0019] The water resistance of a generation film was evaluated from change of the phosphorization object (P=O) seen to the 1250-1300 cm-1 neighborhood. FOSUFO silicate glass (PSG) of 200nm of thickness is deposited on Si substrate, and it is TMS and SiH4 origin. Two kinds of silicon oxides of 400nm of thickness were formed by the used plasma CVD method. As a result of 125 degrees C, two atmospheric pressure, and the pressure-cooker examination of 15 hours estimating, change of P=O was accepted in neither of the samples, but the good result was obtained.

[0020] Next, the result which measured the irregularity of the front face at the time of forming a 4 mm silicon oxide by the CVD which used TEOS and ozone on this film was shown in drawing 8 by using as an underlay film the silicon oxide of 200nm of thickness formed using TMS. The bird clapper is shown to the value with sufficiently small field granularity by the field where an oxygen flow rate is small. The abb sow BANSU ratio of Si-H/Si-OH [in / drawing 5] flow rate / oxygen] in the field of 250 or less seems [is] 3. It is equivalent to the field to cross and this field is suitable as an underlay film of Ozone CVD. The fluidity was accepted in the silicon oxide formed by ozone CVD at this time, and the outstanding covering configuration which has a flattening property in the level difference section was acquired.

[0021] Even if it is except the ozone CVD shown here, you may form the silicon oxide formed by the CVD and the application film forming method for having used the source source of Si of an inorganic system or an organic system on this film, by using as an underlay film the silicon oxide which has Si-H combination.

[0022] As mentioned above, although explained by making the formation method of the silicon oxide by the parallel plate type single cycle plasma CVD method using TMS into an example, you may use a 2 cycle plasma CVD method and bias impression high-density plasma (electron cyclotron-resonance (efficient consumer response), inductance combination type plasma (ICP), helicon wave method plasma, etc. are known as source of plasma CVD by using as Si source the alkoxide which has Si-H combination.

[0023]

[Effect of the invention] According to this invention, a content OH basis is excellent in a moisture transparency prevention property few, the silicon oxide film which has high rank difference covering nature simultaneously can be formed, it is high-density and low-cost manufacture of the semiconductor device which has a multilayer interconnection is enabled.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Explanatory drawing of a plasma CVD room.
[Drawing 2] The infrared-absorption-spectrum view of TMS gas.
[Drawing 3] The infrared-absorption-spectrum view of the reactant gas in plasma CVD.
[Drawing 4] The infrared-absorption-spectrum view of the silicon oxide of this invention.
[Drawing 5] O2 of abb sow BANSU of the molecular binding in a silicon oxide Property view showing a flow rate dependency.
[Drawing 6] O2 of a refractive index n Property view showing a flow rate dependency.
[Drawing 7] The property view showing O2 flow-rate dependency of the etch rate by 0.5% fluoric acid solution.
[Drawing 8] The property view showing O2 flow-rate dependency of the field granularity of TEOS-O3 film formed on the silicon oxide of this invention.
[Description of Notations]
1 | -- A lower electrode, 4 / -- A substrate, 5 / -- RF electrode, 6 / -- The wall of a CVD room, 7 / -- The aperture for infrared observation, 8 / -- Reactant gas exhaust port, 1 -- Gas introduction piping, 2 -- An up electrode, 3

[Translation done.]

* NOTICES *

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2. **** shows the word which can not be translated.
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CLAIMS

[Claim(s)]

[Claim 1] The formation method of the silicon oxide characterized by forming the silicon oxide which is mixed with the source of oxygen and contains Si-H combination by the plasma CVD method by making into the source of silicon the alkoxide which has Si-H combination.

[Claim 2] The formation method of a silicon oxide that the maximum of abb sow BANSU of Si-H of the range of 2100cm-1 [in the infrared absorption of a generation film] on claim 1 publication and [to 2400cm-1 is 1/3 or more] of the maximum of abb sow [BANSU of Si-OH of the range of 3700cm-1 to 3800cm-1].

[Claim 3] The formation method of a silicon oxide that the aforementioned source of silicon is trimethoxysilane in claims 1 or 2.

[Claim 4] The formation method of the silicon oxide which forms a silicon oxide by using the aforementioned silicon oxide as an underlay layer in claims 1, 2, or 3.

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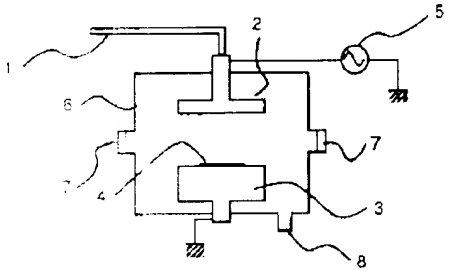
DRAWINGS

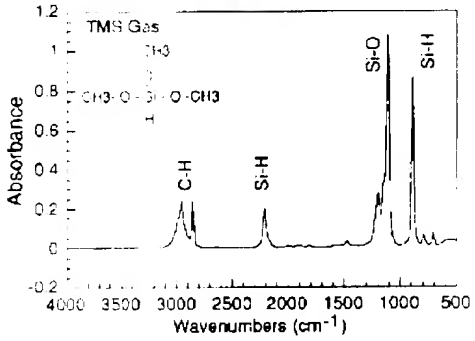
[Drawing 1]

図 1



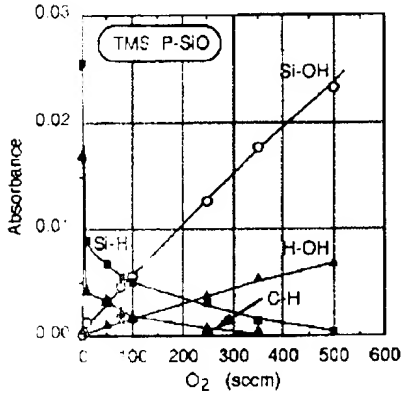
[Drawing 2]

図2



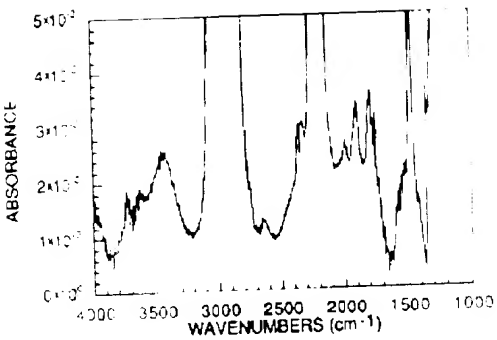
[Drawing 3]

図 3



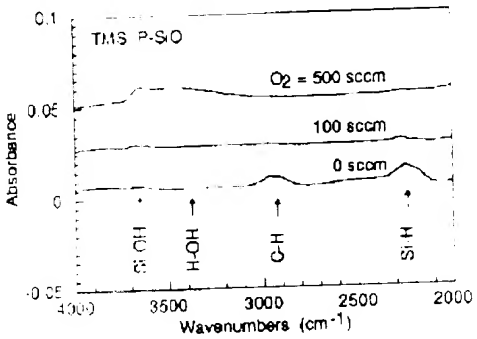
[Drawing 4]

図3



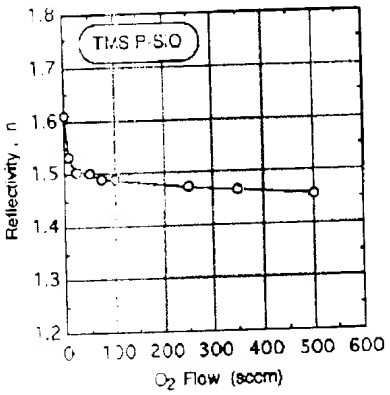
[Drawing 4]

図4



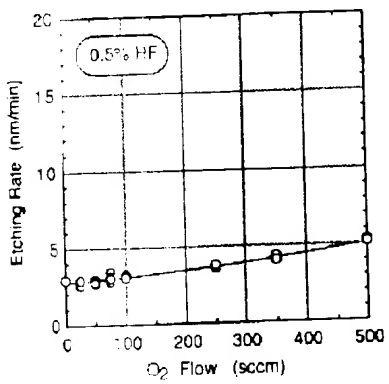
[Drawing 5]

図 6



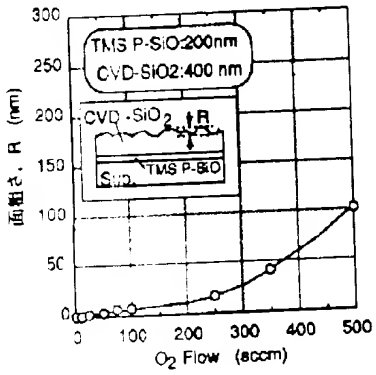
[Drawing 7]

図 7



[Drawing S]

図 8



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